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Theodore A. Rich

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CHARGES ON AEROSOLS

By

(10) Theodore A. Rich

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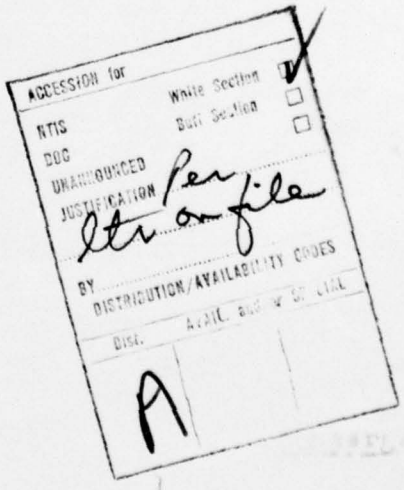
AEROSOL TECHNOLOGY II

Charges on Aerosols

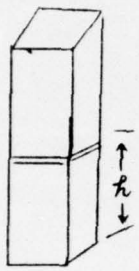
Warning

The emphasis here is on technology not science. Technology is nothing without a scientific precursor and technology only inches ahead without a vigorous scientific background of continuing work. Technology wants to get an answer today: it cannot wait for a unified field theory. It wants answers to practical accuracy. For example, if a multiplicity of equally important factors are involved and are only known to 5% there is little value in knowing that $\pi = 3.14159265$ - for this particular application.

No greater disservice to technology can be made than to imply that the careful distinctions made by science are worthless. Technology makes free use of approximations out of necessity or convenience but never loses sight of the desirability of more basic methods.



The Boltzmann relationship appears so often that a prominent physicist once said that he was prone to believe it applied to anything and that proof was needed that it did not apply rather than the other way around. One familar appearance is in relation of atmospheric density variation with height.



Consider a 1 cm^2 column of air at temperature (T). $P = n\,KT$, $dP = KT\,dn$

the slab (dh) weights $(n\,m\,dh)$ gms

P = dynes cm^2, n = molecules cm^{-3}

m = mass molecule

$$KT\,dn = n\,m\,dh$$

$$\int_{n_o}^{n} \frac{dn}{n} = \frac{m}{KT} \int_{o}^{h} dh$$

$$n = n_o e^{-\frac{mh}{KT}}$$

(mh) is the potential energy of the molecule at (h) and the ratio of $\frac{n}{n_o} = \exp\left(-\frac{\text{potential energy}}{KT}\right)$

The electrical energy is $\frac{Q^2}{2C}$ in a capacitor. Most commercial capacitors of fair size are made by substantial areas of conductors separated by air or some other dielectric, for air:

1) $C = \frac{A}{4\pi S}$ statfarads <u>mutual</u> capacity

S = separation of areas.

An object in space has a <u>self</u> capacitance to ground:

2) for a sphere C = r statfarads (or cm.)

let y = $\frac{\text{electrical energy of (p) electronic charges}}{\text{thermal energy KT}}$

3) $y = \frac{p^2e^2}{2rKT} = \frac{p^2 2.88}{rx10^6}$ $\qquad e = 4.8x10^{-10}KT = 4x10^{-14}(NPT)$

4) $Z = Z_o + 2\,(\,e^{-y} + e^{-4y} + e^{-9y} \cdots\cdots e^{-n^2y}\,)\,Z_o$

This series can be found in Dwight and

5) $\frac{Z_o}{Z} \rightarrow \frac{.95}{(rx10^6)^{1/2}}$ $\qquad$ for $r > 2x10^{-6}$

For particles larger than $r = 2x10^{-6}$cm., this relation (Fig. 1) gives an excellent check with Nolan and Kennan's data taken in 1949. Below $2x10^{-6}$ the results of experiment do not check the Boltzmann equations. It is near this point that the average electrical energy starts to drop off from $^1/_2$ KT. There does not seem to be any good reason why the singly charged particles <u>should</u> have an average energy of $^1/_2$ KT but if this were true

6) $\frac{(Fc)Z(\frac{e^2}{2r})}{Z} = \frac{1}{2}\,KT$ or $Fc = \frac{rKT}{e^2} = .17\ rx10^6$

Fc = fraction of Z particles cm^{-3} that are charged, $\frac{e^2}{2r}$ = electrical energy since capacity of sphere = r cm or statfarads. This does fit the same set of observations (Figure 1). There is a possibility that the check is fortuitous because it would be possible that the sharp cut-off of the Boltzmann relation would be smoothed out by a wide distribution of sizes. There certainly would have been a span of sizes in the test aerosol and there would have been a smoothing effect, (Pollak and Metnieks, On the Validity of Boltzmann's Distribution Law for the Charges of Aerosol Particles in Electrical Equilibrium, Geof. Pura & Appl., <u>53</u>, 1962/III). But for the Boltzmann law to hold either no particles less than $5x10^{-7}$ are hit by ions, or if they are hit (say) by a + ion then almost immediately they should be hit be a negative ion. Neither seems likely.

The history of a single particle might be expected to follow this sequence. At t = o it is assumed without charge and after L_o seconds will be hit by (say) a + ions and become positive. If it is $\sim 10^{-6}$cm and + it will effectively repel another (+) ion and will attract a negative ion in L_+ seconds to become neutral again. On the average after L_o seconds it will be again hit by an ion; it could be of either sign but since the chances are nearly equal it will average out to be a (-) ion and the particle then stays negative for L_- seconds until hit by a (+) ion so the average cycle is

L_o, L_+, L_o, L_- and the fraction of the life of one particle in the charged state is

7) $$\frac{L_+ + L_-}{2\ L_o + L_+ + L_1} = Fc \quad \text{fraction charged.}$$

If we were to make an instantaneous count of the fraction charged of a very large number of such particles that were undergoing this sequence at random then the same Fc holds for the fraction of all the particles that were charged at that instant.

When the particles are larger than 2×10^{-6} a fast + ion can hit a particle already + because it has enough kinetic energy to overcome the repulsive forces. Now it has doubled attraction for a negative ion and is not going to have as long a life as when singly charged. An even larger particle might pick up 3 (or more) charges of the same sign. The ratio of repulsive force (electrical) to the kinetic energy is the controlling factor $\frac{p^2e^2}{2r}$ = electrical energy and $^1/_2 m\ v^2$

is the kinetic energy and so there are grounds for expecting the general relations of eq. 4.

The charge that particles normally carry is due to collisions with "small ions" that exist in the air. These are created in pairs and the population may be in the order of 100 in urban air to over 1000 in rural air.

A molecule with an excess electron is a negative ion; a molecule that has lost an electron is a positive ion. In normal air there are 3 main sources of ionizing radiation - radon which is a gas due to the disintegration of radium in the ground, gamma rays emitted by natural radioactivity of elements in the ground and cosmic rays from outer space. The ionizing radiation knocks an electron off of a molecule (making a positive ion) and the electron is picked up by some other molecule to make a negative ion.

There have been a variety of explanations over the past 50 years of the subsequent behavior. Early theories suspected that the molecular ion collected a cluster of polar molecules and later this fell into disfavor. Recent work by Mohnen seems to be well on the road to general acceptance and experimental proof. Collisions between the molecular ion and other molecules may result in the transfer of the charge from one to another determined by energy considerations. A clustering action then takes place with polar molecules. The cluster is not a permanent configuration; an energetic air molecule can knock off a clustering molecule and other polar molecules can be collected. The most abundant polar molecule is water. The size of the cluster varies with time and at all times there

is a spectrum of cluster sizes. An average value is taken here as that of seven water molecules which will serve the purpose of a general figure to consider the behavior of ions under experimental conditions.

Two ions in space attract or repel one another. The work required to bring two ions from an infinite separation to a distance χ is $\frac{e_1 e_2}{\chi}$ where e is the electron charge = 4.8×10^{-10} statcoulomb and (χ) is the separation in cm. or

$$\text{Potential energy} = 2.3 \times 10^{-19} \chi^{-1} \text{ergs.}$$

The work to separate two ions of opposite sign comes from the thermal energy ($^3/_2$ KT on the average= 6×10^{-14}). The distance at which the average thermal energy is equal to the potential energy is

8) $$6 \times 10^{-14} = 2.3 \times 10^{-19} \chi^{-1}$$

$$\chi = 3.8 \times 10^{-6} \text{ cm.}$$

Two oppositely charged ions at a distance of 3.8×10^{-6} cm. would have a good chance of being pulled together by the electrical forces. The precise probability is difficult to calculate. It will be affected by the speed and relative directions of motion at the time it enters this sphere of influence but there is the relative certainty that one or both of the approaching ions will be hit by air molecules as they approach each other. We can go to experimental results to get another estimate of the "capture size" of the ion.

Experimental results give an average 'birth rate' of ions in normal air:

9) $$q = 10 \text{ ion pair cm}^{-3} \text{ sec}^{-1}$$

The average 'death rate' of ions in particle free air at equilibrium is equal to birth rate

10) $q = \alpha n^2$ where n = ion pair cm^{-3} of the 'population' and $\alpha = 1.6 \times 10^{-6}$ so the average life =

$$L = \frac{\text{population}}{\text{birth rate}}$$

11) $$L = \frac{n}{10} = \frac{q/\alpha}{10} = \frac{2500}{10} = 250 \text{ secs.}$$

A cluster of 7 water molecules would have a mass of

12) $$7 \times \frac{18}{6 \times 10^{23}} = 21 \times 10^{-23} \text{gm}$$

and an average velocity

13) $$\bar{v} = \sqrt{\frac{8KT}{\pi m}} = 2.2 \times 10^{4} \text{ cm/sec}$$

The mean free path would be about

14) $$L = 10^{-6} \text{ cm.}$$

The physical size of the ion, if a cluster of 7 water molecules is certainly small compared to the sphere of influence. (Eq. 8)

If we use eq. 41 of the previous section collisions $sec^{-1} = \pi (r_1+r_2)^2 (v_1^2+v_2^2)^{1/2} Z_1 Z_2$ we can equate this to αn^2 above to get a comparative capture size R_c

$$\pi R_c^2 \left[(2.2 \times 10^4)^2 + (2.2 \times 10^4)^2\right]^{1/2} \times 2500 \times 2500 = 1.6 \times 10^{-6} (2500)^2$$ so

15) $$R_c = 4 \times 10^{-6} \text{ cm.}$$

This is not far from 3.8×10^{-6} obtained from the electrical field considerations. From this it is not a big jump to expect that a singly charged particle around 10^{-6} cm or less would have at least the capture cross-section as the ion since its electrical field is equally effective.

There have been many sophisticated approaches to calculate the coagulation coefficients for ions and particles using spherical models, with trajectories calculated for orbiting ions, grazing ions, impacting ions, etc.. Even the most sophisticated approach has to develop quantities like m.f.p., mobility, mass, etc., which must be shown to check measurement or actual measured values must be used. The following is based on the assumption of the last paragraph above and while far from a rigid demonstration it does seem to be reasonably in accord with the experiment.

The singly charged particle and the ion have a collision rate (β) that would approach (α) if the 'particle' had the same radius as the ion. A substantial number of the ions that approach within 3.8×10^{-6} of the charge on the ion are likely to be captured, a first pass may miss but air molecule collisions may give it several attempts to hit. Assume $\alpha = \beta$ up to $r = 2 \times 10^{-6}$

n_+ = positive ions cm^{-3}

n_- = negative ions cm^{-3}

n = ion pair cm^{-3} numerically $n_+ = n_- = n$

Z_+ = positive particles cm^{-3}

Z_- = negative particles cm^{-3}

$Z_c = Z_+ + Z_-$

Z_o = uncharged particles cm^{-3}

$n_+ \rightarrow n_- = \alpha n_+ n_- = \alpha n^2$ = ion pair lost $cm^{-3} sec^{-3}$ ($\rightarrow$ means colliding with)

$n_+ \rightarrow Z_- = \beta n_+ Z_-$ = loss of charged particle cm ion sec^{-3}

$n_- \rightarrow Z_+ = \beta n_- Z_+$ = loss of charged particle cm ion sec^{-1}

$\beta n Z_c$ = loss of charged particles/sec.

At equilibrium $n_- \rightarrow Z_o = Z_-$ and $n_+ \rightarrow Z_o = Z_+$ and these must be produced at the same rate as $\beta n Z_c$. Since each collision of an ion and a particle means the loss of an ion

16) $q = \alpha n^2 + 2\beta Z_c n$ if $\alpha = \beta = 1.6 \times 10^{-6}$

$= \alpha n^2 + 3.2 \times 10^{-6} \; Z_c n = \alpha n^2 + bnZ$

17) $Z_c = F_c Z$; $F_c = \frac{rKT}{e^2} \approx .1736 \times 10^6$ on the assumption that average electrical energy = $^1/_2$ KT.

$b = 3.2 \times 10^{-6} \times (.174 \times 10^6 r) = .56\, r$

18) $q \approx \alpha n^2 + (.56\, r)\, Zn$

In 1966 Flanagan ran experiments for the equation

$q = \alpha n^2 + bnZ$ and got

$q = \alpha n^2 + (.58 \pm .02)\, r$ (from Fig. 2)

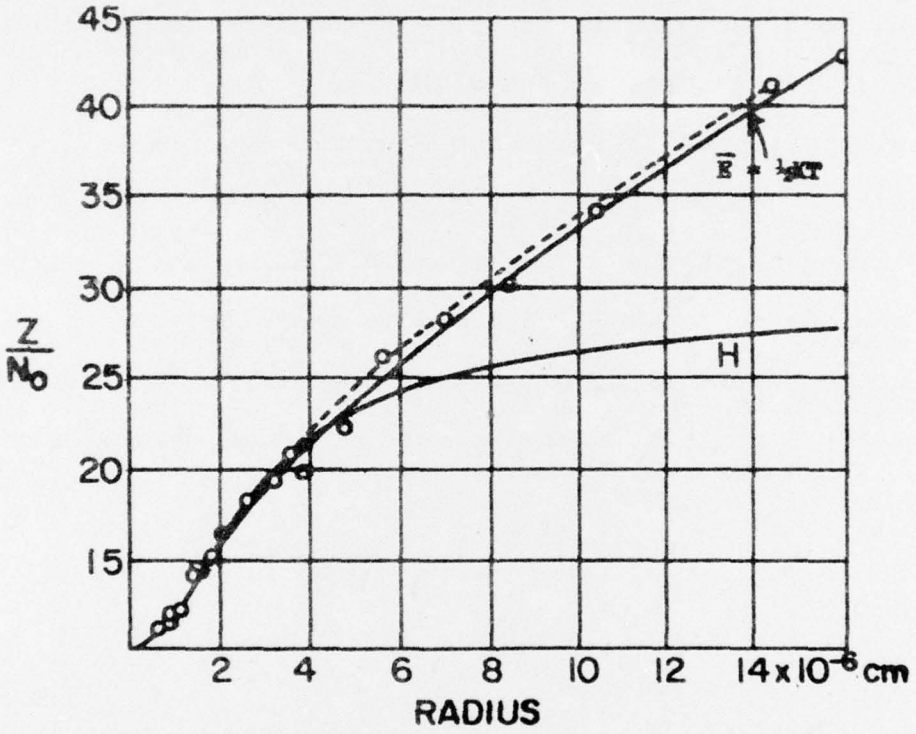
In Figure 1 from Nolan & Kennan's "Condensation of Nuclei from Hot Platinum" in Proceedings of the Royal Irish Academy, 52, 171, 1949, the two relations developed here are superimposed on their observations for the ratio of total particles to uncharged particles. Figure 3 is the summary of fraction of particles charged.

Conclusion

The treatment of fine particle and ion behavior here used is partial and pragmatic. A voluminous, and sometimes confusing, literature is available which will repay the effort of studying it. It should not be expected that any theory is better than the assumptions on which it is based and on the accuracy with which the necessary parameters are known. The ephemeral nature of aerosols and their infinite variety should make one more surprised at the general accord with theory than at the occasional apparently erratic misbehavior. Few people have worked with aerosols without the chagrin of predicting not only the wrong magnitude of an expected change but the wrong sign of the change as well. Welcome to the club!

A second report is in preparation dealing with condensation nuclei meters and the accessories used for size determination.

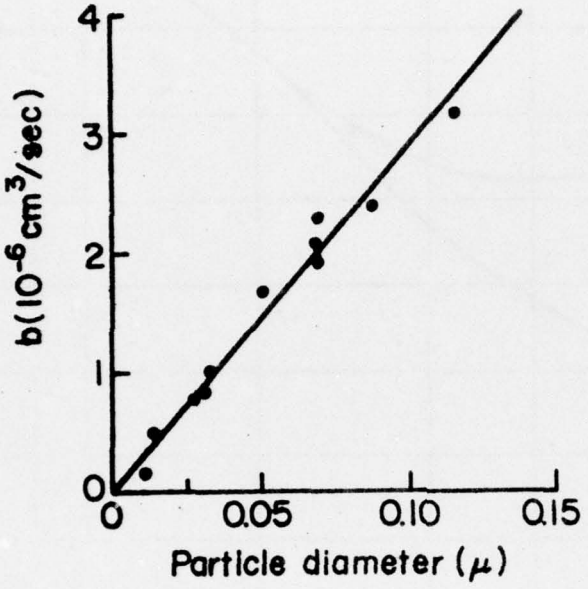
Figure 1



Solid line added to show Z/No for assumption average electrical energy is ½KT for all sizes.

Source: Nolan and Kennan, "Condensation of Nuclei from Hot Platinum", Proceedings of the Royal Irish Academy, 52, 171, 1949.

Figure 2



Source: "Combination of Small Ions with Aerosol Particles," VPV Flanagan, Pageoph, 64, 1966/II.

Figure 3

ELECTRICAL PROPERTIES OF AEROSOLS